Assessment of the FY97 Work on Evaluation of Actinide Migration Studies at Rocky Flats Environmental Technology Site

Points of Major Concern

A. Assessment of the FY97 final report on the evaluation of the actinide migration studies.

1. Concerns are valid about the value of the leaching techniques to Pu extractive leaching.

2. A deficiency in this report is the failure to document sufficiently the procedures used.

3. It is necessary to report the procedures more fully and to document sufficiently the calibrations and the techniques if there is to be adequate quality assurance for data acceptance.

4. It would also be very helpful to the evaluation of the data as well as to increasing confidence in the results if there had been more discussion of the effects of the various leaching steps on plutonium specifically.

5. The age of the hydrolyzed plutonium is a significant factor in the rate at which it can be leached or dissolved from natural materials to which it is sorbed. This could play a significant role in the interpretation of K_d data and in the interpretation of these leaching experiments.

6. There is no description of what is included in the error analysis. This is a matter of quality assurance and it is essential that a proper description of the factors included in the error analysis and that an acceptable factor analysis of the error be provided.

7. Given the differences in the values of duplicate samples from the soil homogenates, it would have seemed necessary to have run many more duplicate samples and even triplicates in some cases.

8. Since, nonhomogeneity in the homogenized samples is offered as the source of the disagreement in the duplicates, it would seem necessary for quality assurance to include some description of the homogenization process and the process used for validation of that process in this system in terms of quality control.

9. On page 12 in the second paragraph the implication is made that the core profiles provide a more reliable measure of the inventory. However, there is no evidence provided to substantiate such a statement. In fact, such a statement would seem to be in strong contradiction to the interpretation of the difference in the duplicates from the sampling as reflecting a strong nonhomogeneity over short distances within the cores.

10. My conclusion is that it is very difficult to accept that the core profile inventory calculations are any more reliable than the homogenate sample calculations and I am not persuaded by the arguments provided in the report as the data simply do not support those arguments sufficiently.

11. It does not seem likely that this data can be used due to the problems with reproducibility and the inability to explain strong variations.

12. It would seem very important to obtain a better understanding of whether the problems with duplicate samples is due to poor homogenization or is reflecting extreme heterogeneity.

13. If any data from these studies are to be used in modeling for performance assessment of remediation strategies, the reports must be more concerned with validating QC and QA.

B. Conceptual Model

1. There is need for information on colloid size distribution as well as the soil porosity to colloids, which perhaps, could be achieved by appropriate column elution measurements using soil samples.

2. In the discussion on page 5 of K_d values that there is the assumption of kinetic exchange between the solid and liquid phases. This should be validated as frequently such exchange may not be complete in both directions due to redox, precipitate formation etc.

3. On page 6 it is stated that erosion is the most important process for transport of Pu. If this is a correct statement, the question arises of the value of K_d measurements.

4. The conceptual model seems to be a valid approach, but careful analysis should be given to the types of data needed to validate the important transport processes to be modeled. The experimental program should be focused on obtaining an adequate and validated data base for those mechanisms.

C. Path forward

1.There should be a strong emphasis on reproducible and, therefore, reliable values for a number of duplicate samples. Until values can be duplicated, any data from such studies are not sufficiently reliable to be used in modeling.

2. There is little, if any data, on remobilization which is extremely important since the ability to leach Pu by very strong acid redox treatment may have little meaning in terms of mobility in nature.

3. Given the lack of reproducablity on the relatively few duplicate samples that have been run, either a much better sampling technique is needed or many more samples need to be analyzed before a reliable database to use in a conceptual model can be established. In addition, there should be a significant experimental effort to ascertain if erosion or diffusion are the principal mechanisms for actinide migration. The conceptual model should also be carefully analyzed to ascertain what should be the extent and validity of the data set needed to obtain reliable values of migration.

Assessment of the FY97 Work on Evaluation of Actinide Migration Studies at Rocky Flats Environmental Technology Site

The primary focus of this assessment was the final report entitled "Actinide Migration Studies at the Rocky Flats Environmental Technology Site" by B. D. Honeyman and P. H. Santschi. In addition, the conceptual model and plans for further studies connected with the conceptual model as well as the actinide migration studies are reviewed.

I. Assessment of the FY97 final report on the evaluation of the actinide migration studies.

The work included in this report involved determination of the phase speciation of plutonium in certain soils as well as an evaluation of the mass loading of plutonium in three ponds. In addition, the measurement of K_d values for Pu and U(VI) with soils was included. It was stated that the scope of the work had as overall objectives to provide a preliminary determination of the Pu phase speciation and the range of soil distribution coefficient (K_d) values in the pond area soils and determine the plutonium inventories for the ponds. The work conducted was directed to the overall objectives listed. However, it is important to note that these were termed "preliminary" measurements. This is an important qualification as the data is rather limited and the interpretation of the data rather uncertain. This is best viewed as an important but quite preliminary study to providing the type of data that would be needed to take advantage of the conceptual model being developed. In the succeeding discussion, the final FY97 report is assessed in the same sequence as the topics are presented in the report.

At the bottom of page 2 the report provides a satisfactory justification for the selection of the sites sampled. Again it should be noted that the relatively small number of sites as well as the quite limited number of samples from each site reflects the "preliminary" aspect of this study. The authors have used a rather standard approach of selective leaching from soil samples by increasingly aggressive chemical treatment. This can be a concern when applied to actinide studies since the behavior, particularly of plutonium, does not follow that of many of the systems typically studied in such geochemical leaching procedures. For example, the chemistry of Pu(IV) is quite different than that Fe(III) or Mg(II). It is worth noting that the procedures selected are standard in the geochemical leaching systems and the PIs indicate their understanding of the problems in interpreting data from the selective extractions on pages 5-7 where they provide a quite good discussion of these problems. The presence of this discussion adds to confidence in their ability to more properly interpret these results. Nevertheless, concerns are valid about the value of these techniques to Pu extractive leaching.

A deficiency in this report is the failure to document sufficiently the procedures either in the brief discussion in the text on pages 3 and 4 or in the appendices. It would seem essential to provide such a level of quality assurance. For example, in Appendix 3 there is a note about using a PEG treatment, but no reference or other information. There is a reference to "step 11" but there is no step 11 in the procedure. Later in that same procedure use of a resin is mentioned, but

there is no indication whether they are speaking of cation or anion resin, mesh size, cross linkage, etc. These are all properties of major significance in any quality control system. That same appendix tells of addition of lanthanum carrier, but the concentration is not given although the volume is. Similarly, it describes collection of a sample on filter paper, mounting the filter paper on a planchette, and then (presumably) counting. However, there is no description of how the counting efficiency was determined for alpha emitting nuclides with such "thick" samples. This is a very important aspect of any quality control system and should be well documented in such a report. In fact, the type of counting system used for the alpha emitters is not described. On page 5 of the text, they state that the experimental protocol followed for "quantifying" the dissolved phase plutonium activities is outlined in Appendix 3, but the outline is far too brief and no such quantification procedure is described nor even mentioned. Similarly in Appendix 4 it is stated that the U(VI) is counted by a liquid scintillation method. Again, there is no description of the counter, the counting cocktail, the calibration procedure, etc. involved in this process. Appendix 1 does specify that anion resin is used in that procedure and alpha pulse analysis is used in the counting. Presumably this is also true for Appendix 3, but it should be specifically stated. Again since lanthanum carrier is added they are dealing with a thick sample for pulse height analysis and the effect of the thickness on the analysis should be described as well as the calibration procedure followed.

Table 1 is confusing as a number of alkali and alkaline earth chloro compounds are listed under the title Exchangeable. In the text no explanation of the meaning of those compounds is provided. It is also not clear what the other entries under the titles of this table mean as those systems are not specified as such in the procedures. Presumably these are alternate leaching processes, but the purpose of Table 1 is certainly unclear and the result is confusing. It would also be very helpful to the evaluation of the data as well as to increasing confidence in the results if there had been more discussion of the effects of the various steps on plutonium specifically. For example, NH_2OH can reduce Pu(IV) to Pu(III) which could increase its solubility. Of importance is that approximately 96% or more of the Pu was obtained only by the most severe chemical leaching under the organic and residue fractions. In connection with that value, it should be noted that this work used a 0.45μm filter size. It has been well demonstrated in many studies that this filter size fails to capture many Pu colloids. Successively finer filtration reduces the Pu to extremely low "dissolved" concentrations. Therefore the 96% can not be considered to reflect that 4% of the Pu is truly dissolved since the severe treatment can result in the production of colloid particles finer than the 0.45μm. This should be more emphatically noted in the evaluation of the results.

In the middle of page 9, above Table 2 the association of Pu with organic matter is discussed. In fact whether the organic matter is soluble under the range of treatment is not particularly significant as a major effect of the humic materials, that are the major constituents of natural organics, is to reduce plutonium to the tetravalent state in which it hydrolyzes, but does not complex directly with the humates. The resulting hydrolyzed plutonium is very likely to be bound to colloidal particles. It is also rather well documented that much of the suspended or colloidal humic material is in the form of pseudo colloids in which the humic macro molecule is

bonded around an inorganic clay or iron hydroxide type of particle. In turn, the hydrolyzed plutonium can be sorbed to this humate layer and effectively move with the migration of the humic pseudo colloid. However, there is no evidence that Pu(IV) would bind the humics in neutral waters where hydrolysis is very strong.

Another aspect of this leaching process that is important to note in connection with the evaluation of the leaching procedures is that the hydrolyzed Pu(IV) may experience important aging effects. The resulting oxopolymers are much more resistant to dissolution even by very strong acid conditions. Usually, oxidation to Pu(VI) state is required which may take some time. Consequently, the age of the hydrolyzed plutonium is a significant factor in the rate at which it can be leached or dissolved from natural materials to which it is sorbed. This could play a significant role in the interpretation of K_d data and in the interpretation of these leaching experiments.

It is unfortunate that more duplicate samples were not available particularly for the residual fraction. The reproduciblity of the results as reflected in the duplicate sampling is cause for concern. However, the reproduciblility is even poorer for the pond soil samples and further comment on reproducibility is reserved until that discussion.

On page 10, concerns on the interpretation of the selective leaching analysis due to the redox nature of plutonium is briefly discussed. This is a very important point and it is unfortunate that the phraseology suggested in the middle paragraph on page 10 where the interpretation is limited to "certain fraction of plutonium" is not used throughout the report as this is an aspect of the data that must be constantly kept in mind, particularly for anyone not thoroughly familiar with Pu behavior.

In summary, the results of the sequential leaching indicate that the plutonium is quite insoluble and only the harshest treatments will leach any significant fraction. While quantitative interpretation and the use of such data in the conceptual model analysis may be difficult, the semiquantitative assessment is that the solubility of Pu or the migration of Pu (except by erosion processes of soil movement) will be very limited and probably of little concern.

The section of the report on the problem with the analyses of the pond sediments is a concern. The data is listed to two decimal points (four significant figures) in many cases, however, little error analysis is provided. Also, there is no description of what is included in the error analysis. Again, this is a matter of quality assurance and it is essential that a proper description of the factors included in the error analysis and that an acceptable factor analysis of the error be provided. This is particularly important given the large discrepancy in the duplicate sampling reported in Appendix 7. Errors provided are approximately 5% of the values and yet duplicate values differ by as much as 300%. It would seem that the errors listed are probably only from counting, which is not acceptable. Moreover, given the differences in the values of duplicate samples from these homogenates, it would have seemed necessary to have run many more duplicate samples and even triplicates in some cases. At present, the values obtained from

these studies on the pond sediments are highly questionable due to the large discrepancies in the duplicate samples. The same concern over error analysis is involved in appendices 8 and 9 and in Figure 2. The strange variations for the values in those figures may reflect the errors as again quite small uncertainties are listed for values with very large differences. Until validation of the error that would include the various factors involved in the experiment is available, an assessment of the interpretation of the data is not possible. An indication of the concern that arises from the disagreement between duplicates is found at the bottom of page 10 where the value of 1266.7 is quoted for sample B506A as the one measure of the range of values. However, the duplicate measurement from that same sample is only a value of 410.8. In fact, the 1266.7 value seems to be the more questionable since it is much higher than any other values measured. Similarly, the other extreme of the value of 91.3 which is quoted contrasts sharply with its duplicate sample value of 148.3. Both of these examples would indicate that the uncertainty is perhaps as high as 50% of these values. If that is true, any discussion of the range is meaningless unless if it is conducted within the range of the uncertainties. This concern about the uncertainties is also reflected in Figure 2 where any interpretation of those curves must be based on a realistic evaluation of the total experimental uncertainty of each value.

The problem with the reproducibility of the duplicate samples is addressed on page 11 where it is suggested that it is due to nonhomogeneous dispersion throughout the environmental medium. However, if these are two samples from the same homogenized system, it is difficult to see why there would be factors of 2 to 3 discrepancy between such measurements. If the heterogeneity explanation has any validity, a much better system of homogenization should be used. If there is such extreme nonhomogeneity in the environmental media, many more samples are needed to allow any reasonable validation of the inventory of the ponds. Since, nonhomogeneity in the homogenized samples is offered as the source of the disagreement in the duplicates, it would seem necessary for quality assurance to include some description of the homogenization process and the process used for validation of that process in this system in terms of quality control.

The problem with this explanation of the nonhomogeneity within the homogenates is seen in the next paragraph on page 11 in which the discussion for the difference in the values of the inventories obtained from the homogenates in the core profiles assumes truly homogenous samples. There seems to be a contradiction in using the results from the homogenized samples when they are attributing the disagreement between duplicate samples to a lack of homogeneity. If indeed the interpretation of nonhomogeneity within the homogenized samples is a valid explanation of the disagreement in the duplicates, that data is essentially useless in terms of obtaining inventory values. Similarly, if the problem is sampling rather than nonhomogeneity in the homogenates, a serious question arises whether the core sampling is reliable. On page 12 in the second paragraph the implication is made that the core profiles provide a more reliable measure of the inventory. However, there is no evidence provided to substantiate such a statement. In fact, such a statement would seem to be in strong contradiction to the interpretation of the difference in the duplicates from the sampling as reflecting a strong nonhomogeneity over short distances within the cores. Consequently, core samples could be substantially

nonhomogeneous from one site to the next. Given the small number of cores taken this would indicate a strong uncertainty for any value obtained for the inventory from the core sample analysis. It is also stated that a difference between the homogenates in the core inventory calculations may reflect the shallow penetration of the cores taken from the homogenates. Since no explicit values are given for the depth of penetration for the homogenate samples, this statement cannot be validated by the data provided in the report. In general, from Figure 2 if it is accepted that the few high points are unreliable, it would seem that most of the Pu lies within the top five or 10 centimeters. My conclusion is that it is very difficult to accept that the core profile inventory calculations are any more reliable than the homogenate sample calculations and I am not persuaded by the arguments provided in the report as the data simply do not support those arguments sufficiently.

The values in Tables 3, 4 and 5 have no significance unless estimates of the net uncertainties are included for all values. This should not be simply the counting error, but the total estimated error. Without such errors these tables cannot be used with any degree of confidence.

The section on the K_d values is introduced with a very useful discussion of the limitation and justification for such K_d measurements.

On page 15, on the 3rd line it is stated that Pu interacts more strongly with dissolved organic matter than with particles. This statement does not find support from any data in this report and no reference is cited. Hydrolyzed Pu will have a tendency to be sorbed to macro molecular humic particles through either colloid or pseudo colloid type formation. However, whether this would happen to a greater degree than similar physical sorption to suspended or colloidal clay particles etc. is not proven. The statement could be true for the trivalent state in a reducing medium, but for oxic waters it should be qualified for proper understanding and proper references cited.

On page 16, Table 7 includes errors which range from 4 to 300%. Some statement should be provided as to how those errors were obtained and what is included in their analysis. Also with such very large errors on some of the values, their use to calculate the fraction dissolved would result in very large uncertainties which should also be noted in the text. In Appendix 3 it is stated that the filtration for obtaining the K_d values uses 0.4 micron filters. As discussed earlier, the solubility measured by filtration has been found in other studies to be strongly dependent upon the size of the filter used and, therefore, this represents the solubility related to that size filter which would allow smaller colloidal particles with sorbed plutonium to pass and be registered as dissolved plutonium. Any interpretation of the data has to take that aspect into account. It would also be worth having some comment on why the pH increased in all cases over the five-day period of the experiment. The statement that the K_d values may represent a lower limit because of the high solution to solid ratio is puzzling. That should result in a larger uncertainty and, therefore, in a larger error. But, within that error, the values should not be so sensitive to such a ratio. Presumably, this uncertainty is reflected in the errors listed in Table 7.

The desorption kinetics experiments seem to have been well conducted and it is notable that the K_d data is much more consistent. While a proposal is made for interpretation of the decrease in K_d values with depth, it would be useful to measure the ratio of silica to clay with depth to validate the proposal.

It is stated that the sorption kinetic data provided no statistical difference in the K_d values over a 6 day period. A table of such data should be provided to validate this statement for quality assurance.

In summary, these experiments provide a useful and valuable initial set of data for development of a database for the conceptual model validation. However, it does not seem likely that this data can be used due to the problems with reproducibility and the inability to explain strong variations. If, indeed, these variations reflect extreme heterogeneity within samples and, therefore, within soils, before any conceptual model analysis is possible, many more data points would be needed. Therefore, it would seem very important to obtain a better understanding of whether the problems with duplicate samples is due to poor homogenization or is reflecting extreme heterogeneity. This would seem to be the most important question at this time from the 1997 results. Additionally, if any data from these studies are to be used in modeling for performance assessment of remediation strategies, the reports must be more concerned with validating QC and QA.

II. Conceptual model

The proposed conceptual model seems to include all the factors that are needed to provide satisfactory assessment of actinide migration at the Rocky Flat site. However, the model does require reliable data and, therefore, a prime consideration is that sufficient experimental values of sediment and water samples be available to ensure a valid data base of sufficient extension and validity.

The total inventories probably can be sufficiently well estimated by good measurements of soil samples. However, the rate of transport may differ in different media so the migration rate is much harder to estimate with confidence. Most (> 95%) of the Pu would be transported by colloid movement with water flow; however, such colloid migration varies with colloid size as well as with soil porosity (i.e., there could be filtering of larger particles). There is need for information on colloid size distribution as well as the soil porosity to colloids, which perhaps, could be achieved by appropriate column elution measurements using soil samples. In this connection I would note line 5 from the bottom of page two which say "ranges of transport rates" must be known "for the various mechanisms" to estimate reliable proportions of actinide transport by each mechanism. In this regard R_c may be the most important factor over the long time period while R_i may be more important over the shorter period of the first few decades.

It also should be noted in the discussion on page 5 of K_d values that there is the assumption of kinetic exchange between the solid and liquid phases. This should be validated as frequently such exchange may not be complete in both directions due to redox, precipitate formation etc. The degree of reversibility could also vary with time due to the increased insolubility of the hydrolyzed plutonium polymers. The effects of size of hydrolyzed plutonium is noted in the second paragraph from the bottom on page 5.

On page 6 it is stated that erosion is the most important process for transport of Pu. If this is a correct statement, the question arises of the value of K_d measurements. These are more relevant to colloid sorption in transport than to erosive movement of soil.

In summary the conceptual model seems to be a valid approach, but careful analysis should be given to the types of data needed to validate the important transport processes to be modeled. The experimental program should be focused on obtaining an adequate and validated data base for those mechanisms.

III. Path forward

The comments to follow are based on the review of the Honeyman/Santchi 1997 final report. It would seem necessary to do more "speciation" studies. There should be a strong emphasis on reproducible and, therefore, reliable values for a number of duplicate samples. Until values can be duplicated, any data from such studies are not sufficiently reliable to be used in modeling. If there is a problem with the homogenization process, a new process should be developed. Top priority should be given to obtaining reliable values that are interpretable using appropriate numbers of duplicate samples for QA. Further, Pu in the waters at the sampling sites should also be measured for the Pu content as this could give some indication of the relationship between the K_d values and the soil water distribution in C2.

The earlier studies found most of the plutonium in the organic and residue fractions. There is little, if any data, on remobilization which is extremely important since the ability to leach Pu by very strong acid redox treatment may have little meaning in terms of mobility in nature.

In summary, given the lack of reproducablity on the relatively few duplicate samples that have been run, either a much better sampling technique is needed or many more samples need to be analyzed before a reliable database to use in a conceptual model can be established. In addition, there should be a significant experimental effort to ascertain if erosion or diffusion are the principal mechanisms for actinide migration. The conceptual model should also be carefully analyzed to ascertain what should be the extent and validity of the data set needed to obtain reliable values of migration.

In summary, I would return to the important word in the beginning of the final report and emphasize that the studies this far can only be evaluated as "preliminary." At this point it seems

very difficult to ascertain the extent of sampling that is needed or the reliability of the successive leach procedures and of the K_d measurements in terms of applicability of the resulting data to the conceptual model.

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